

Department of Metallurgy
Massachusetts Institute of Technology
Cambridge, Massachusetts

FACILITY FORM 802

N65-82873

ACCESSION NUMBER

30

(PAGES)

CP 57317

(NASA CR OR TMX OR AD NUMBER)

(THRU)

(CODE)

(CATEGORY)

UNPUBLISHED PRELIMINARY DATA

PROGRESS REPORT

for the period

July 15, 1964 - January 15, 1965

Grant NsG-117-61

UNPUBLISHED PRELIMINARY DATA

To

National Aeronautics and Space Administration
Washington, D. C.

DISPERSION STRENGTHENED SYSTEMS

This report covers the six-month period from July 15, 1964 - January 15, 1965, for work undertaken on the following topics:

1. Internal Oxidation of Copper-Nickel-Aluminum Alloys
2. Nickel-Thoria and Nickel-Molybdenum-Thoria Dispersion Strengthened Alloys Produced by Selective Reduction of Oxides
3. Structure Stability and Properties of Nickel-Thoria and Nickel-Molybdenum-Thoria Alloys Produced by Selective Reduction of Mixed Oxides
4. Oxide Dispersion Strengthened Niobium Alloys
5. The Role of Recrystallization and Stored Energy on the Strength and Ductility of Oxide Dispersion Strengthened Iron
6. High Volume Intermetallic Compound - Ductile Phase Composite Structures
7. Beryllium Oxide Dispersion Strengthened Iron Alloys
8. Mechanism of Deformation and Fracture of Metal-Metal Oxide Systems

A paper, entitled, "Alumina Dispersion Strengthened Copper-Nickel Alloys", based on the research conducted by Michio Yamazaki, is currently being reproduced in preprint form. It is hoped that this will be available for mailing within two weeks.

Two other papers are being prepared for preprinting, and will also be submitted as soon as they are available.

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1. INTERNAL OXIDATION OF COPPER-NICKEL-ALUMINUM ALLOYS

It was the aim of this phase of our program to study internal oxidation, not of a pure metal base, but of a solid solution strengthened matrix. In the past, work had been done on the internal oxidation of both copper and nickel, each containing small quantities of an oxidizable element, such as aluminum, beryllium, silicon, titanium, and chromium. In an effort to try to increase the low temperature strength properties, while retaining or improving the high temperature properties of the pure metal base, a series of copper-nickel-aluminum alloys were prepared as fine powders and internally oxidized, followed by extrusion into bar stock. These alloys were based on copper, and contained as a solid solution strengthener 10, 20, and 30 weight percent nickel, each alloy containing from 0.75 to 0.85 aluminum as the element to be converted to oxide form; this amount of aluminum yields about 3.5 volume percent of Al_2O_3 after oxidation.

Variables in the experimental program included powder size and shape, method of powder milling and preparation, method of internal oxidation, and extrusion ratio.

The strength values at room temperature were significantly better than those obtained for copper-aluminum oxide alloys; recrystallization was delayed to temperatures well over $1000^{\circ}C$, and up to $1050^{\circ}C$; and creep-rupture properties at $650^{\circ}C$ were as good or better than those achieved in mechanically mixed copper-aluminum oxide alloys containing considerably higher oxide content, but were not as good as the results obtained with an internally oxidized copper-3.5 volume percent oxide alloy produced by internal oxidation. The stress versus rupture time and stress versus minimum creep rate plots were extremely flat at $650^{\circ}C$, fully confirming the extremely good structure stability indicated by the high temperature annealing test used to detect recrystallization.

The previous semi-annual report covered most of the details of this program more completely, and such data will not be repeated in this case. In addition, the work has now been prepared as a technical report, and is being submitted for publication. Preprint of this report will be mailed within a month.

2. NICKEL-THORIA AND NICKEL-MOLYBDENUM-THORIA DISPERSION STRENGTHENED ALLOYS PRODUCED BY SELECTIVE REDUCTION OF OXIDES

This work, too, was covered in considerable detail in the previous six-month summary report and will not be repeated in this instance. The results of the work were presented at the Powder Metallurgy Joint Group in London, October, 1964. As soon as reprints are available, they will be submitted. Preprints have already been delivered to NASA.

3. STRUCTURE STABILITY AND PROPERTIES OF NICKEL-THORIA AND NICKEL-MOLYBDENUM-THORIA ALLOYS PRODUCED BY SELECTIVE REDUCTION OF MIXED OXIDES

Because it is possible to obtain cheaply the pure oxides NiO and MoO_2 , and because it is an easy and inexpensive process to comminute such oxides to a particle size as fine as 0.2 micron, this seems like an unusually attractive process for producing high strength, oxide dispersion strengthened systems which may be based either on a pure metal, such as nickel, or on an alloyed matrix, such as nickel-molybdenum, nickel-tungsten, etc.

In the program recounted under item (2), above, and in succeeding work which measured the high temperature stability of these alloys, it was evident that significantly higher room temperature strength properties were achieved than had been expected, and lower higher temperature stability was indicated than had been expected. A detailed analysis indicated that somewhere in the powder and compact processing steps, water vapor had either been retained, or had been picked up by the fine thoria particles which are hydroscopic, leading to oxidation of the nickel and nickel-molybdenum alloy matrices. The presence of ultra-fine nickel oxide or molybdenum oxide would contribute to the low temperature properties but would sharply decrease the high temperature properties. A decision was made to extend this work, taking increased precautions to avoid water pick-up from the atmosphere or any form of oxidation of the very fine high reactive nickel and molybdenum powders in the reduced form. It was expected that the room temperature properties would decrease; the 1800°F creep rupture properties would increase beyond the already attractive levels; and significant gains would be made in structure stability above 2000°F.

For this purpose, two new alloys have been prepared; the first of these is a nickel-2.5 volume percent thorium alloy, and the second is a nickel-12 percent molybdenum-9 volume percent thorium alloy.

Nickel-2.5 volume percent thorium composition - nickel oxide of 0.2 micron average particle size was ball milled for two hours in an ethyl alcohol - thorium nitrate mixture, containing enough thorium nitrate to produce 2.5 volume percent of thorium. The thermal decomposition temperature in the vacuum phase of the cycle was raised from 650 to 750 - 800°C to avoid retention of water vapor from the decomposition of the thorium nitrate. Subsequent oxide reduction was carried out at 900°C compared to 800°C in previous trials, to guarantee more complete reduction of the nickel oxide.

A modified extrusion can was designed which permitted the 900°C hydrogen reduction treatment to be carried out with the loosely compacted alloy powder in the can. Without removal from the can, the ends were sealed off, thus assuring complete protection against rehydration of the super-fine thorium.

In order to allow for subsequent cold working treatments, this product was extruded at a relatively low reduction ratio, namely, 3:1. This was just adequate to densify the alloy and to preserve the oxide distribution so that subsequent cold work and cold work plus annealing treatments could be carried out.

The properties of this nickel - 2.5 volume percent thorium alloy are now under study. Because of the sensitivity of the room temperature hardness measurements after various high temperature annealing treatments as an indication of recovery, recrystallization, and general alloy stability, these studies were carried out first on this alloy.

Figure 1 shows the change in Vickers hardness number after annealing times of 1 and 5 hours at temperature for this alloy and several of the alloys produced earlier in the program. These older alloys include N-1, nickel-3.5 volume percent thorium, N-3, nickel-9 volume percent thorium, and NM-3, nickel-12 percent molybdenum-9 volume percent thorium.

The results for the new nickel-2.5 volume percent thorium alloy show a low as-extruded hardness value, as would be expected from the low extrusion ratio utilized in the consolidation process. More important, however, is the fact that this alloy shows no hardness drop until after

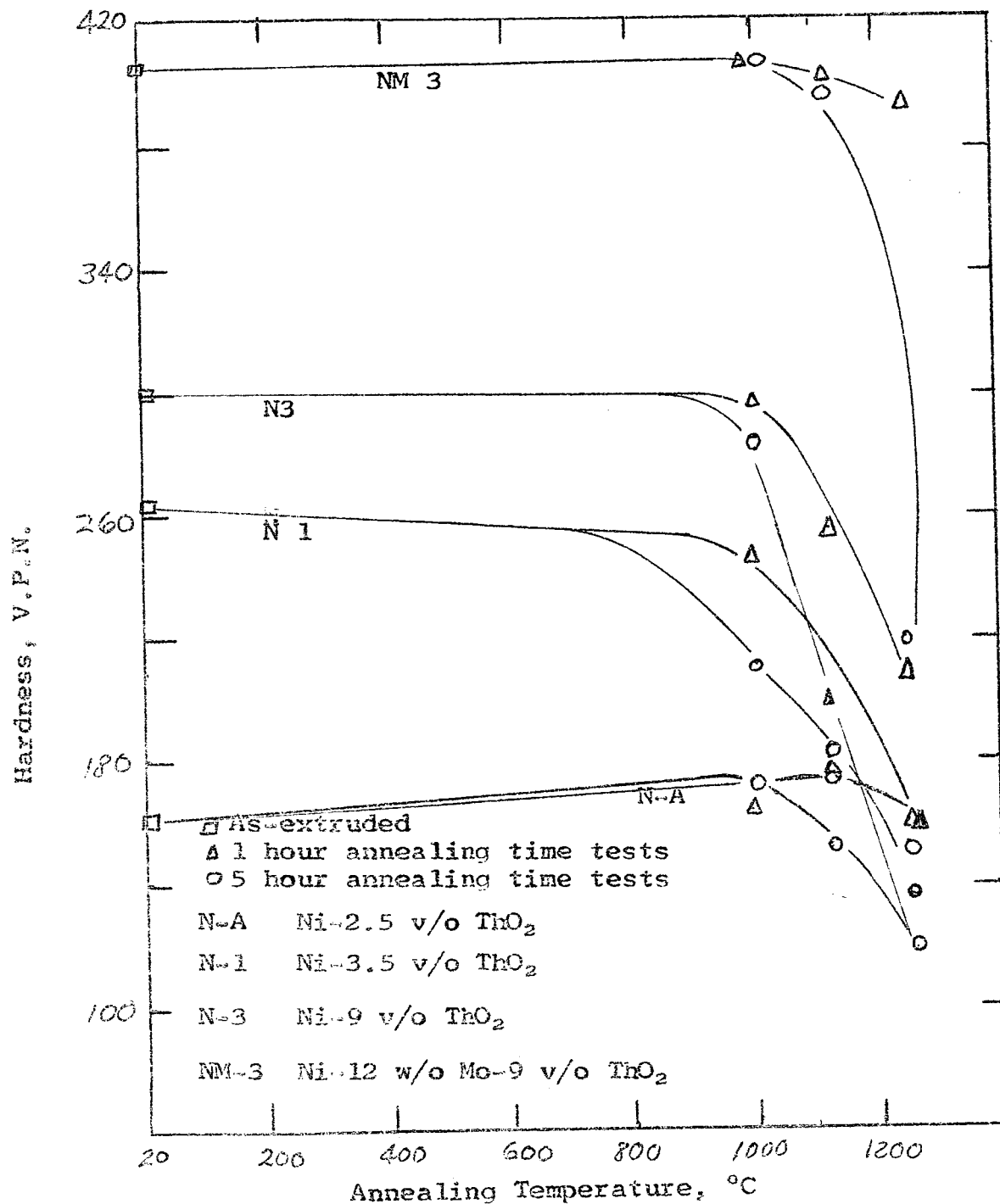


Figure 1. Change in room temperature hardness as a function of 1 and 5 hour annealing treatments of nickel and nickel-molybdenum alloys dispersion strengthened with thorium.

1100°C has been reached, at which point it has values approximately the same as it had at room temperature. In fact, after one hour at 1250°C the alloy exhibits only a very small decrease in hardness compared to its room temperature value. Compared to alloys N-1 and N-3, it is very evident that this new alloy shows greater stability both in the 1 and 5 hour tests at temperatures beyond 1000°C.

This alloy will now receive increasing amounts of cold work with and without intermediate annealing steps, to see how high the high temperature strength and ductility values can be raised, and to examine benefits at room temperature. Also to be conducted are a series of X-ray diffraction studies to establish the nature of the structure, looking for preferred orientation, and evidence of recrystallization.

Nickel-12 percent molybdenum-9 volume percent thoria - this, the second of the two alloys, was prepared from considerable finer nickel and molybdenum oxide powders than was the case for NM-3 (see above). Both powders were separately ground to 0.2 micron, average particle size; the powders were then mixed and ball milled for two hours in an ethyl alcohol - thorium nitrate solution. The decomposition and hydrogen reduction steps were the same as those used for the new nickel 2.5 volume percent thoria alloy, with the added modification that argon was eliminated during the selective reduction step to avoid introducing water vapor by this means.

This alloy is now ready for extrusion, after which tests for alloy stability and properties will be undertaken.

4. OXIDE DISPERSION STRENGTHENED NIOBIUM ALLOYS

The systems niobium-alumina and niobium-thoria were selected in an effort to see if reactive metals can be oxide dispersion strengthened, and if so, to which maximum temperatures the structures would remain stable. In the one case aluminum oxide was selected as the dispersoid since it is readily available as the product Alon C, the gamma alumina form, in a particle size between 0.01 and 0.03 micron. Dry blending of the niobium and alumina powders was utilized. In the case of the niobium-thoria alloy, the thoria was derived from decomposition of a thorium nitrate salt in an alcohol solution.

In both cases, the niobium was available as niobium hydride, and was received as 7 microns powder particles.

The niobium-alumina alloy was prepared by conventional dry mechanical mixing, followed by compaction, decomposition of the hydride, and extrusion as described in previous reports. Some bar stock was produced in the extrusion step, however, the yield of material was poor.

Room temperature tension tests were performed on the as-extruded specimens, yielding ultimate strength values of 156,000 psi with a ductility of 2.5 percent elongation. By comparison, the tension strength of pure niobium is reported to be between 60 and 80,000 psi. The observed difference between pure niobium and the alumina dispersion strengthened niobium is obviously due to the retained cold work of extrusion.

Stress rupture tests were also run, in an argon atmosphere, at 1800°F. The results are shown in Table I.

Table I
Stress Rupture Properties of a Niobium-Alumina Alloy at 1800°F
in Argon

Stress, psi	Life, hrs.	% Elong.	% Red. of Area
20,000	0.17	47.8	59.4
16,000	1.0	57.2	61.0
13,000	5.6	36.8	52.1
10,000	34.7	46.5	49.5
8,000	111.1	24.9	23.0 (tapered specimen)

A comparison of these properties with those for pure niobium indicates that this alloy has comparable strength values to that of pure niobium in short time tests at high stresses, but poorer values at the lower stresses. The fractured specimens indicate copious formation of voids in the 1800°F tests, and efforts are under way to establish the source of these voids.

Hardness tests were also measured at room temperature as a function of a one-hour annealing treatment at temperatures up to 3632°F (2000°C), the tests being conducted in vacuum. The results are shown in Table II.

The increase in hardness to 3272°F (1800°C) is also observed in pure niobium and is probably associated with impurity pick-up. It was observed that at 2192°F (1200°C) and above, a surface oxide was formed which increased in hardness with increasing temperature. The oxide was identified as being predominantly Nb_2O_5 .

Table II

Room Temperature Hardness as a Function of Annealing Temperature for
Nb-Al₂O₃

Temperature		VHN
°F	°C	
392-1832	200-1000	366
2192	1200	389
2552	1400	389
2912	1600	389
3272	1800	426
3632	2000	138

Tests are planned to establish whether the niobium interacted with the aluminum oxide, possibly reducing it, in part, at the higher annealing temperatures. The specific technique to be utilized has not yet been established.

Photomicrographs of the alloy after high temperature exposure show a very coarse structure, but light microscopy is not adequate to establish the nature of this structure.

Niobium - thoria alloy - The dispersion strengthened niobium-thoria was prepared in two different ways because of anticipated difficulties during the decomposition of thorium nitrate salts, which were expected to lead to oxidation of the decomposed niobium hydride starting powder. Accordingly, the two procedures used were the following:

1) Prior decomposition of thorium nitrate to produce thoria, and subsequent mechanical mixing of the thoria produced in this manner with niobium hydride.

2) Ball milling of niobium hydride with thorium nitrate in an ethyl alcohol solution, followed by evaporation of the alcohol and vacuum removal of the nitrous oxide and water vapor resulting from the thorium nitrate decomposition.

Both of these methods were discussed in the previous semi-annual report.

The dry-mixed niobium-thoria alloy was evaluated by means of Vicker's hardness measurements at room temperature following annealing treatments of 1 - 5 hours at temperature intervals from 1500 - 2200°F (816 - 1204°C). Table III shows the results.

Table III
Change in Hardness as a Function of Annealing Time and Temperature for
Mechanically Mixed Niobium-Thoria Alloys

<u>Specimen</u>	<u>Temperature</u>		<u>VHN</u>
	<u>°F</u>	<u>°C</u>	
<u>as-extruded</u>			413
1 hr.	1500	816	389
	1800	982	377
	2000	1093	382
	2200	1204	439
3 hrs.	1500	816	397
	1800	982	360
	2000	1093	334
	2200	1204	398
5 hrs.	1500	816	343
	1800	982	342
	2000	1093	391
	2200	1204	419

Laue back-reflection X-ray photographs indicate that the observed decrease in hardness is due to recovery and partial recrystallization of the structure. The subsequent increase in hardness is due to oxygen contamination, but whether this oxygen comes from the atmosphere or from reduction of the aluminum oxide by niobium is as yet undetermined.

Test specimens are being prepared of this alloy and will be evaluated both in room temperature tension and high temperature creep rupture shortly.

The alloy prepared by milling of the components in alcohol is ready for compaction, after which it will be extruded and also tested by similar techniques to those discussed above.

In the coming months, it is planned to try to answer the following questions:

- 1) How stable are the alumina and thoria dispersions in niobium as a function of increasing temperature and time?
- 2) Are oxygen and nitrogen being picked up by the niobium; if they are, are these elements coming from the atmosphere, or from decomposition of the refractory oxide?
- 3) What are the maximum temperature and time at temperature for stability of these two oxides in niobium?

5. THE ROLE OF RECRYSTALLIZATION AND STORED ENERGY ON THE STRENGTH AND DUCTILITY OF OXIDE DISPERSION STRENGTHENED IRON

One of the biggest riddles, subject to a number of different explanations, is the question of how important is the stored energy of cold work on the strength of oxide dispersion strengthened alloys, and on ductility. Of equal interest and complexity is the question of what happens if one recrystallizes an oxide dispersion strengthened alloy without at the same time destroying the oxide dispersion existing in the structure.

To try to answer these questions, iron was selected as the base material for the following important reasons:

- 1) Iron has a transformation temperature at about 910°C. This low transformation temperature permits one to extrude iron-refractory oxide mixtures either in the ferritic state or in the austenitic state; in the former instance, the extruded product should end up in the cold worked or strained condition; in the latter instance, the structure should end up completely recrystallized because the oxide dispersion cannot suppress the transformation from gamma to alpha.

- 2) It should be possible to take the cold worked or recrystallized structures and treat them in such a way that the recrystallized material is subsequently cold worked (in the alpha state), and the strained structure can be recrystallized by heating into the gamma range.

This has been done in a series of four iron alloys containing alpha and gamma aluminum oxides, and thoria. The oxide contents were at two levels: 2.5 volume percent content (alpha alumina and thoria), and 10 volume percent (alpha and gamma alumina).

Most of the room temperature tension tests, the 1000, 1200, and 1400°F stress rupture tests, and hardness versus annealing temperature tests have been completed. These data are being analyzed in detail, and will be presented formally as a doctorate thesis.

Within several months, it is anticipated that the data will be reviewed, and condensed in the form of a technical report which will be submitted to NASA as part of our program.

Preliminary results appear to indicate that recrystallization in the absence of structural changes (change in oxide interparticle spacing) do not harm the high temperature creep rupture properties of

iron, this effect being more evident at 1400° than at 1000°F.

The low oxide content iron alloys are readily amenable to further cold work, such cold work leading to improved low and high temperature properties. If, instead of continuously cold working the material, one cold works in small steps of 10 to 15 percent, and utilizes intermediate annealing treatments which lead to recovery but not to recrystallization, further increases are noted in both low and high temperature strength properties, with attendant improvements in ductility. These results tend to confirm work reported in the literature on low oxide content materials, notably nickel-thoria alloys. The total plasticity is amazingly high in spite of relatively low tension ductility values.

In the higher oxide content materials, where the interparticle spacing is considerably finer, the benefits of subsequent cold work and annealing treatments are minimized, because recovery and recrystallization take place very much more slowly in such structures. Further, the additional amount of cold work which can be introduced is relatively small compared to that for the low oxide content materials.

Preliminary examination of the data indicates that creep in these alloys does not follow a fourth power relationship versus stress as was indicated in earlier work by Weertman, and Lenel and Ansell; instead, it appears that an exponential law is followed.

It is anticipated that a model can be proposed describing the role of stored energy, not in terms of total energy content, but in terms of distribution and intensity of cold work in relationship to the oxide particle distribution.

5. HIGH VOLUME INTERMETALLIC COMPOUND - DUCTILE PHASE COMPOSITE STRUCTURES

Work is continuing on the evaluation of high volume content intermetallic compound - ductile binder composite materials produced by powder metallurgical methods. In earlier work four single phase alloys with compositions lying in the NiAl phase field were produced and tested, as were alloys made from mixtures of NiAl (74 weight percent nickel) and various ductile metal and alloy binder powders.

An additional series of alloys based on Ni₃Al, and one based on CoAl were also produced. Nickel-7.1 weight percent aluminum solid solution binder was used for the Ni₃Al alloys, and both pure cobalt or

a cobalt-5.3 weight percent aluminum solid solution binder were used for the CoAl alloys. The compositions of these alloys are listed in Table IV. The purpose in using solid solution binder alloys containing aluminum was to minimize interaction between the binder and the hard phase. In the system Ni-Al, Ni_3Al is in equilibrium with a Ni(Al) solid solution; in the system Co-Al, CoAl is in equilibrium with a Co(Al) solid solution.

Table IV
 Ni_3Al and CoAl Base Alloy Compositions

Alloy	Composition (by volume)				
	% Ni_3Al	% Ni sol.sol.	% CoAl	% Co	% Co sol.sol.
Ni_3Al	100				
$\text{Ni}_3\text{Al-NiSS}^*-15^+$	85	15			
$\text{Ni}_3\text{Al-NiSS-30}$	70	30			
CoAl-Co-30			70	30	
CoAl-Co-40			60	40	
CoAl-CoSS-20			30		20
CoAl-CoSS-30			70		30

* SS stands for "solid solution"

+ indicates weight percent of binder phase

Results - Electron photomicrographs of as-extruded Ni_3Al and CoAl base alloys were made using a two-step replication technique. The structures of the Ni_3Al alloys with 15 and 30 volume percent binder consisted of a dispersion of fine (~0.1 micron) particles of Ni_3Al surrounded by the binder. A few larger particles of Ni_3Al were also present.

The CoAl alloys consisted of CoAl particles ranging in size from 0.1 to 10 microns dispersed in and separated by a thin layer of binder. There was considerable elongation of the intermetallic CoAl particles in the extrusion direction.

Stress rupture tests were performed on the Ni_3Al and CoAl base alloys in air at 982°C (1800°F). The results of these tests are listed in Tables V and VI and plotted in Figures 2 and 3.

Table V
Results of Stress Rupture Tests on Ni₃Al-Base Alloys

Alloy	Test Temp. °C	Stress, psi	Rupture life hrs.	Red. A. %	Elong. %
Ni ₃ Al	982	7,000	0.082	13.6	18.3
		5,000	0.225	18.1	15.1
		3,200	4.15	11.6	9.4
		2,000	91.7	7.2	7.3
Ni ₃ Al-NiSS-15	982	15,000	0.086	19.2	11.4
		10,000	1.61	16.0	5.7
		7,000	31.8	6.7	4.6
		5,500	229.5	4.9	2.3
Ni ₃ Al-NiSS-30	982	15,000	0.228	1.5	4.1
		10,000	1.9	9.7	3.5
		6,500	32.2	4.3	2.3
		5,000	175.3	-	9.1

Table VI Results of Stress Rupture Tests on CoAl-Base Alloys					
Alloy	Test Temp. °C	Stress, psi	Rupture life hrs.	Red. A. %	Elong. %
CoAl-CoSS-20	982	14,000	2.95	5.3	4.3
		10,000	8.06	7.0	5.3
		4,500	307.0	21.0	19.3
CoAl-CoSS-30	982	20,000	0.124	7.6	3.9
		12,000	2.035	-	3.6
CoAl-Co-30	982	13,000	0.022	-	5.6
		11,000	0.09	5.7	3.7
		10,000	0.14	-	5.5
		8,000	0.63	3.0	4.4
		6,000	1.53	4.0	5.2
		4,000	6.16	8.3	6.2
		2,500	27.3	6.8	9.0
CoAl-Co-40	982	15,000	0.006	7.0	8.6
		13,000	0.032	4.2	7.5
		10,000	2.59	9.4	3.2
		7,000	1.48	5.6	5.6
		6,000	1.56	5.6	3.7
		5,000	3.9	4.3	5.0
		3,000	39.5	2.9	4.9
		2,500	500.0*	1.4*	0.9*

*Test discontinued

The rupture curves for Ni_3Al with binder lie considerably above those for pure Ni_3Al . The reasons for this are not known but may be due to differences in fracture mechanism in the presence of a binder. The value of 6000 psi for a 100-hour rupture life for the Ni_3Al -30 percent Ni solid solution, at 1800°F, is very good.

The stress rupture results for CoAl base alloys show that a cobalt-aluminum solid solution binder gives better properties than the pure cobalt binder. Two reasons for this can be advanced. First, the cobalt-aluminum solid solution is more nearly in equilibrium with CoAl; secondly, diffusion processes associated with high temperature creep and fracture, such as microcrack and void growth and dislocation climb, are slowed considerably in the solid solution binder phase. The best of the Co-Al base alloys has about the same strength as the best Ni_3Al base alloy.

It should be noted that for the CoAl-Co-30 alloy there are two tests that lasted far longer than the extrapolation of shorter time data indicates they should have. One explanation for this is that these specimens were free of flaws or weak areas. Alternatively, alloying of a beneficial nature may be occurring in the binder phase in the long time tests. Metallographic examination of the fractured stress rupture specimens revealed a tendency toward fine microcracking in very short-time tests, and void formation and growth in the longer time tests. These microcracks are probably present either as very small flaws in the as-extruded material or represent fractures of weak areas very early in the creep test. At longer times these cracks round out and grow by diffusion, minimizing stress concentration effects.

Two types of hardness annealing tests were run on representative alloys. In one type, specimens were heated for one hour in vacuum at increasing temperatures. In the other, specimens were held for increasing times at 982°C (1800°F) in vacuum. The results of these tests on CoAl-Co-30 and Ni_3Al -NiSS-15 are given in Tables VII, VIII, IX, and X, and are plotted in Figures 4, 5, 6, and 7.

For alloy CoAl-Co-30, increasing the temperature for a constant annealing time does not have the same effect as increasing the time at constant temperature (see Figures 4 and 6). This is due to the fact that this alloy passes into the CoAl single phase region from the two-phase region at about 2000 or 2100°F. This is the point where an

Table VII

One-Hour Room Temperature Hardness Annealing Data for CoAl-Co-30

<u>Temperature, °C</u>	<u>Vicker's Hardness, hc/mm²</u>
as-extruded	731
1000	751
1200	763
1400	718
1600	695
1800	669
2000	633
2100	619
2200	632
2300	645
2380	573
2400	548

Table VIII

One-Hour Room Temperature Hardness Annealing Data for Ni₃Al-NiSS-15

<u>Temperature, °C</u>	<u>Vicker's Hardness, hc/mm²</u>
as-extruded	762
1000	753
1200	755
1400	758
1600	747
1800	719
2000	673
2200	629
2400	587

Table IX

Hardness - Time Annealing Data for CoAl-Co-30 at 1800°F

<u>Time (hours)</u>	<u>Vicker's Hardness, hg/mm²</u>
0	731
.25	664
.628	660
1.00	669
2.50	634
15.8	616
75.1	614
150.1	591

Table X

Hardness - Time Annealing Data for Ni₃Al-NiSS-15 at 1800°F

<u>Time (hours)</u>	<u>Vicker's Hardness, hg/mm²</u>
0	731
1.0	719
1.61	693
31.8	685
229.7	636

upward inflection is noted in Figure 4. The decrease in hardness above 2300°F is associated with severe void formation in the single-phase alloy.

The gradually decreasing hardness with increasing time and temperature, aside from the peculiarity in the behavior in CoAl-Co-40, is probably due to recovery and loss of the cold work of extrusion held in the binder. The hardness values of pure CoAl and Ni₃Al are only 535 and 633 kg/mm², respectively. It is not likely that a simple mixture of either intermetallic with a soft, unhardened matrix could yield a higher hardness than the pure intermetallic compounds.

Three point transverse rupture bend tests were performed at room temperature on three alloys. The results of these tests are listed in Table XI.

Table IX
Transverse Rupture Bend Test Results

<u>Alloy</u>	<u>Rupture Modulus</u> <u>10³ psi</u>	<u>Young's Modulus</u> <u>10⁶ psi</u>
CoAl-Co-30	248.5	26.6
CoAl-Co-30	239.0	26.0
CoAl-Co-30	268.0	26.0
CoAl-Co-40	264.0	27.3
CoAl-Co-40	308.0	24.5
Ni ₃ Al-NiSS-15	363.0	30.3

In all cases no plastic deformation was measured; due to the nature of the tests, however, several percent of plastic flow could have occurred in the most highly stressed areas and gone undetected. It should be noted that the rupture strength values measured in these tests are close to the yield strengths predicted from the hardness readings by plasticity theory:

$$\frac{P}{A} = 3 \bar{Y}$$

where: P = hardness load

A = area of hardness impression

\bar{Y} = yield stress.

These values are compared with the averages of the measured transverse rupture values in Table XII.

Table XII

Calculated and Measured Rupture Strength Values

Alloy	Calculated Yield Stress (10^3 psi)	Measured Rupture Modulus (10^3 psi)
CoAl-Co-30	346.0	251.8
CoAl-Co-4	354.0	286.0
Ni ₃ Al-NiSS-15	361.0	363.0

The hardness test is essentially a compression test; the transverse rupture test is a bend test in which one side of the specimen is subjected to tension and the other to compression stresses. The yield stress calculated from a hardness reading is a compression value. The strength that is measured in a transverse bend test is a tensile strength since fracture initiates at the tension side of the specimen. In a brittle material the tensile strength is lower than the compression strength, sometimes by as much as a factor of eight.

In the case of the two CoAl-base alloys tested, the rupture moduli are less than the calculated yield stresses. The effectiveness of the binder is shown by the fact that while the calculated yield stress of the high binder alloy is only slightly higher than that of the low binder alloy, the measured rupture modulus is significantly higher.

The calculated and measured values for Ni₃Al-NiSS-15 are equal (Table XII). While this does not suggest a large amount of ductility, it does show that there was no premature brittle fracture in the elastic region due to notches or internal stress raisers.

Qualitative observations of the surfaces of stress rupture samples indicated good oxidation resistance. To check this an oxidation test was performed on a sample of CoAl-Co-30 in air at 982°C (1800°F). The results showed a weight gain of 0.6 mg/cm² after 100 hours exposure compared to 1.6 for Nichrome for the same conditions, an extremely low amount of oxidation. Additional tests are being made.

Summary - A good separation of hard phase particles by ductile binder has been achieved by the technique of dry ball milling the constituent powders, followed by loose powder (unsintered) extrusion.

Stress rupture and hardness annealing tests indicate some retention

of the stored energy of extrusion.

A solid solution alloy binder yields high temperature strength properties superior to those achieved with a pure metal binder.

Transverse rupture tests indicate that the ductile binder is effective in preventing premature brittle fracture but does not result in measurable plastic flow.

Future Work - A series of interrupted creep tests are under way to check the mechanism of high temperature fracture in the CoAl and Ni₃Al base alloys. Additional transverse rupture tests are planned, some on annealed samples to determine if low temperature strength and ductility can be improved by relief of the cold work of extrusion. Oxidation tests will be run on representative alloys of the NiAl and Ni₃Al base types. It is anticipated that this phase of our program will be completed very shortly.

7. BERYLLIUM OXIDE DISPERSION STRENGTHENED IRON ALLOYS

Little work has been done on the oxide dispersion strengthening of body-centered-cubic metal; most of the work in the past has been concentrated on the close-packed face centered-cubic metals. Iron, and iron base materials remain as extremely interesting structures which could be benefited a great deal by oxidation dispersion strengthening; the ferritic structures stand to benefit most because of the relatively low strength values of the body-centered-cubic structures compared to the close-packed face-centered cubic and hexagonal structures.

In earlier work with aluminum oxide in iron, there was the problem that iron oxide contamination resulted in the formation of iron aluminate spinels. In similar work with thorium dispersion strengthened structures, the problem of water vapor pick-up by the ultra fine thorium was encountered. It was decided that beryllium oxide would be a particularly desirable refractory oxide; not only because of its high melting point, but also because of its low specific gravity, absence of phase transformations, and absence of spinel formation with iron oxide.

The initial phases of the program have been concerned with techniques which might lead to the most ideal distribution of beryllium oxide in iron. A number of techniques are being tried, and it is hoped

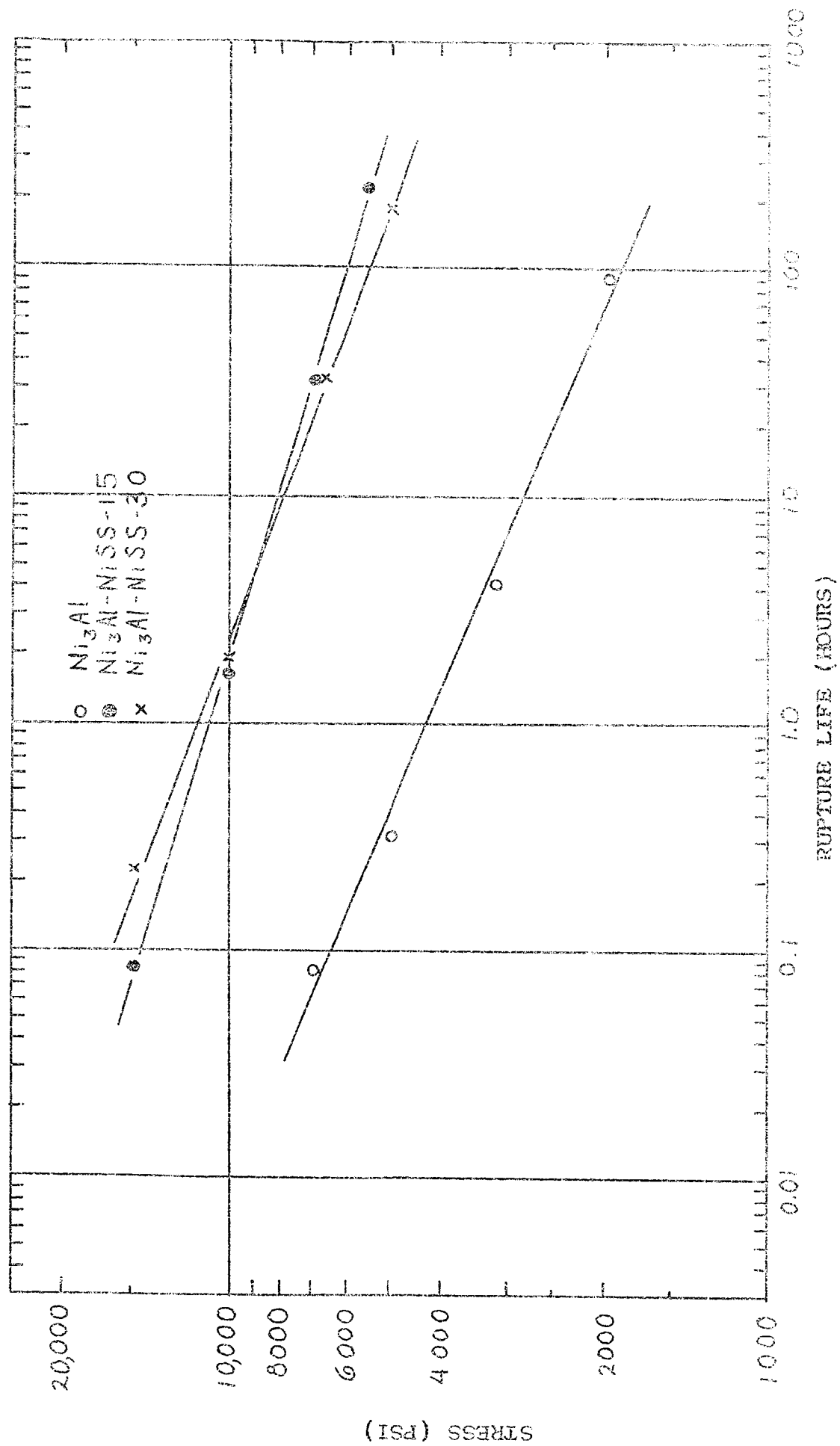


Figure 2. Stress rupture results of Ni_3Al base alloys at 982°C (1800°F)

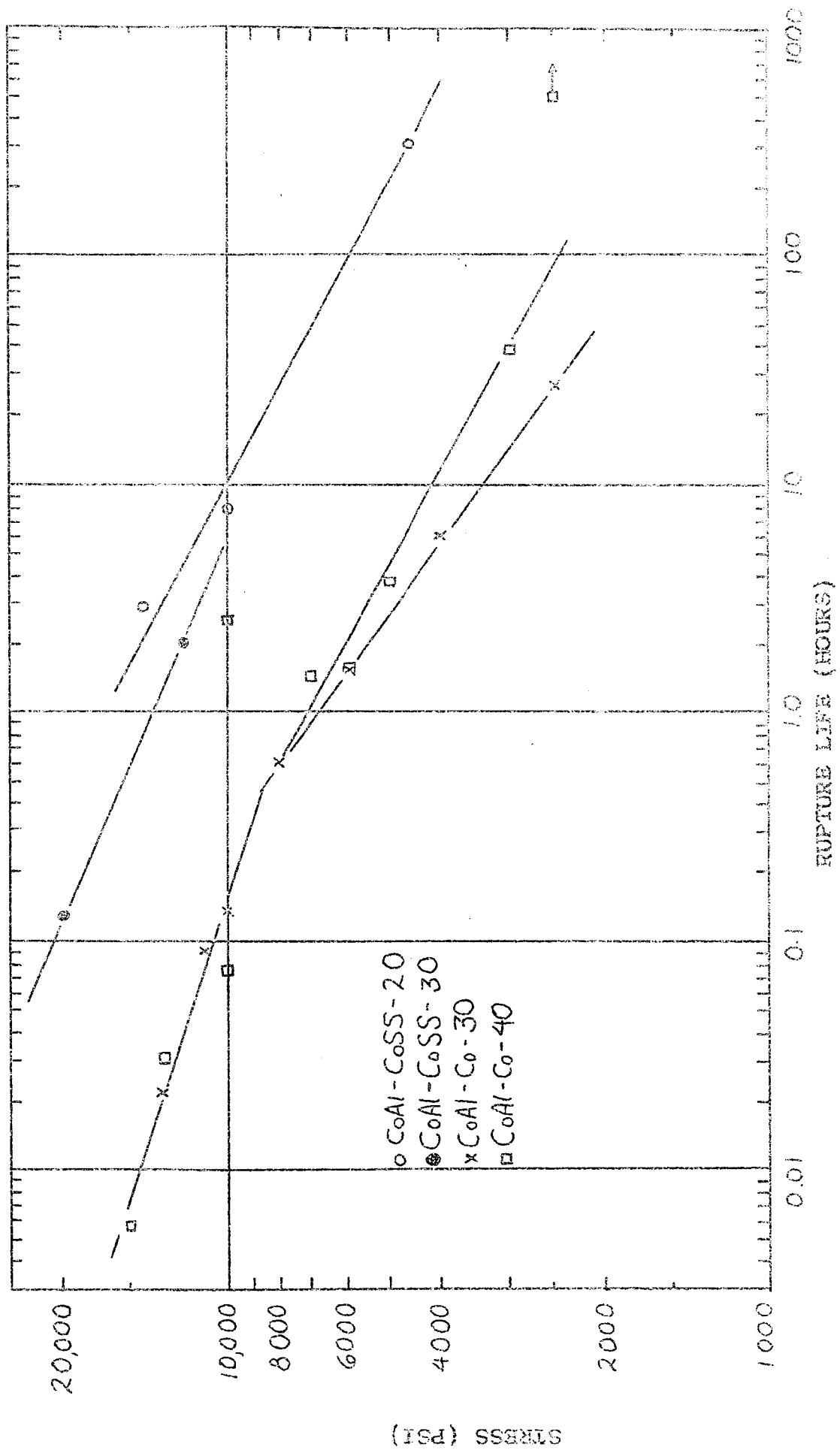


Figure 2. Stress rupture results of CoAl base alloys at 999°C (1960°F)

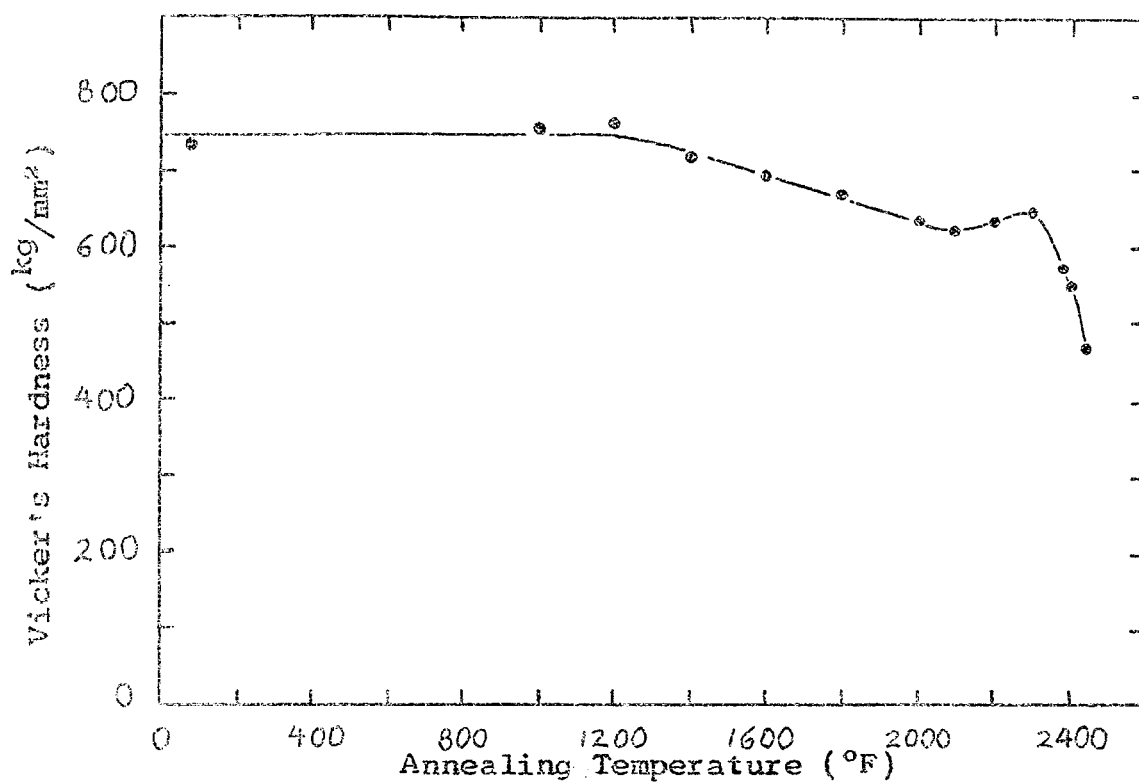


Figure 4. One hour hardness for annealing curve for CoAl-Co-30

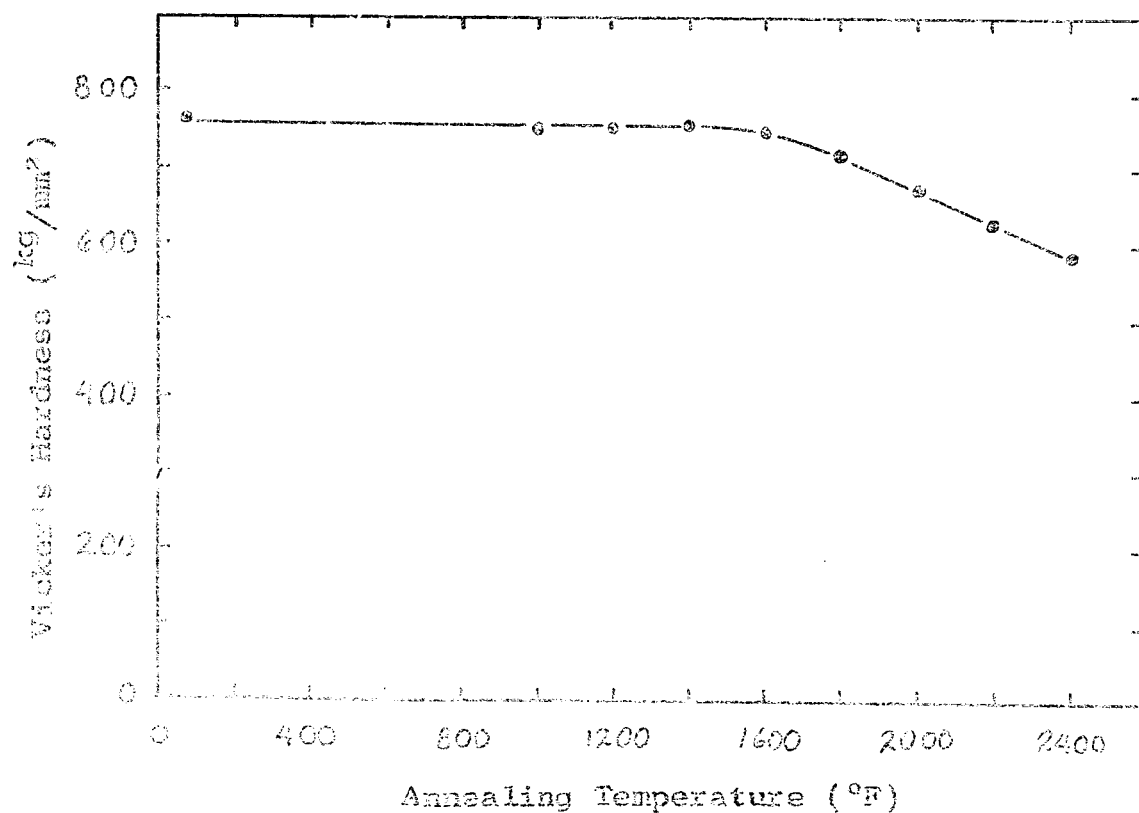


Figure 5. One hour hardness annealing curve for Ni₃Al-NiSS-15

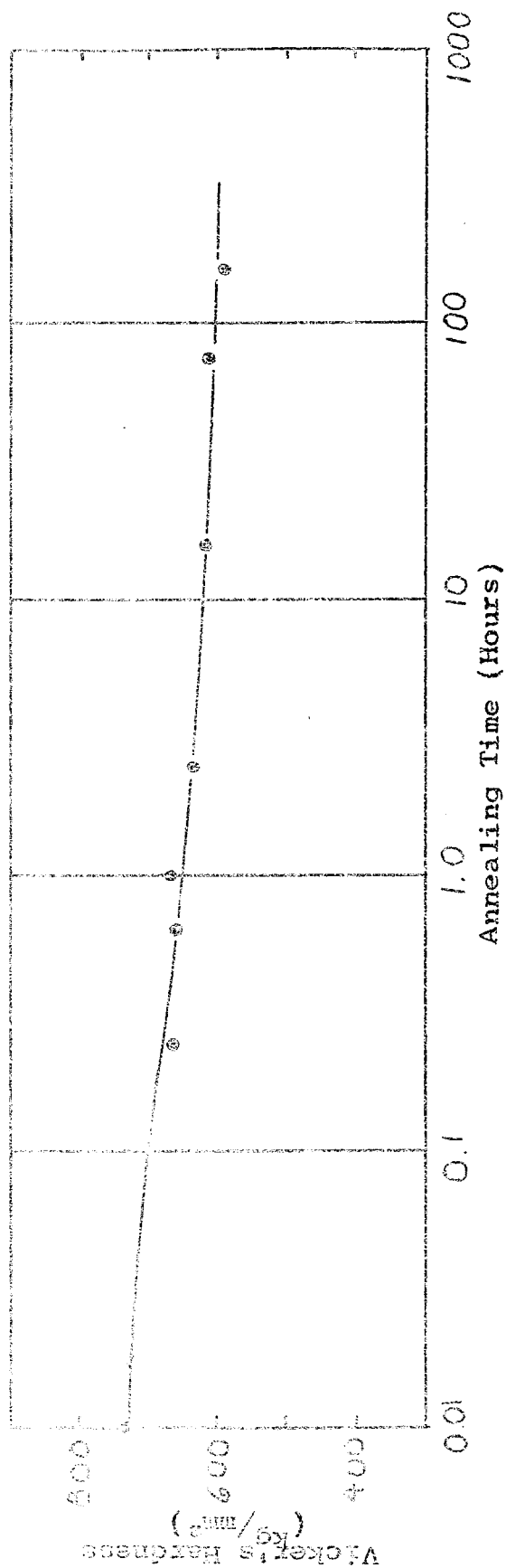


Figure 6. Hardness annealing time curve for CoAl-Co-30 at 982°C (1800°F)

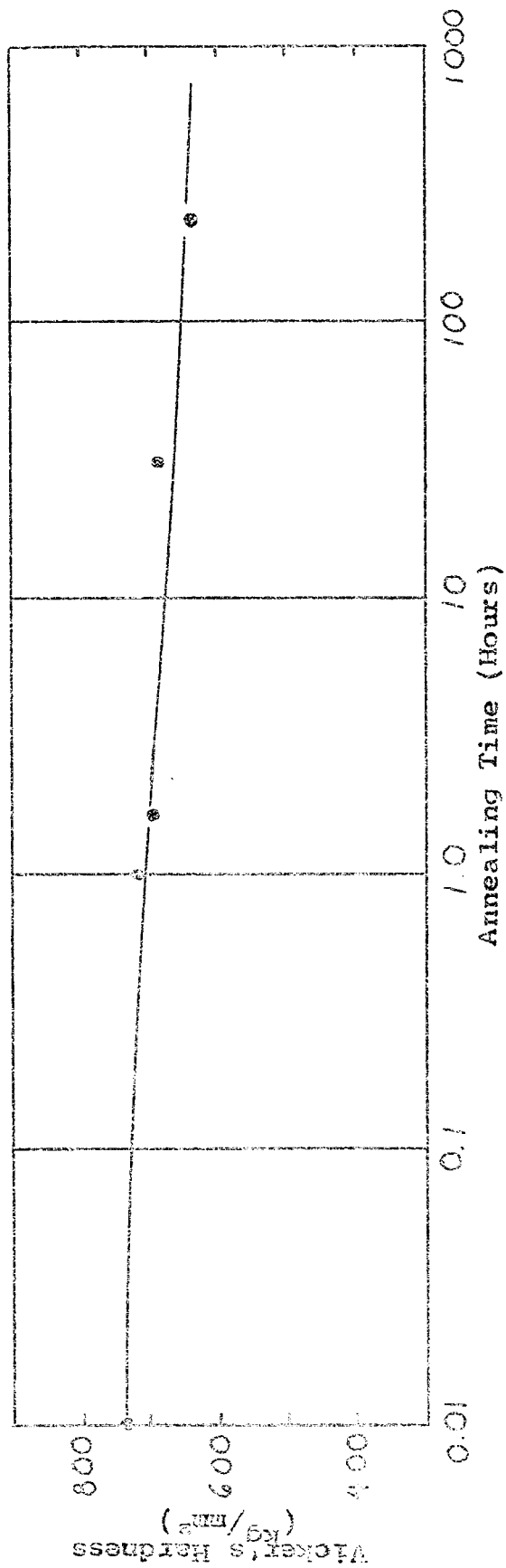


Figure 7. Hardness annealing time curve for Ni₄Al-NiSS-15 at 982°C (1800°F)

from these to select the one which will lead to the most ideal distribution of beryllium oxide in the iron matrix. The methods are the following:

- 1) Internal oxidation of iron-beryllium solid solution compositions
- 2) Diffusion of beryllium into an iron matrix containing a finely dispersed iron oxide
- 3) Formation of an iron oxide - beryllium oxide composite with subsequent reduction of the iron oxide

There seems little doubt that internal oxidation can be carried out successfully, and for this purpose, a series of iron - beryllium alloys have been produced containing the following amounts of beryllium in weight percent: 0.48, 1.35, 2.52, and 4.64. These alloys are presently being comminuted into fine powders for subsequent internal oxidation.

Because of the known low solubility of oxygen in iron at the (lower) temperatures of interest for internal oxidation, coupled with the realization that low oxygen solubility and low oxygen diffusion rates would lead to formation of relatively coarse BeO particles, there has been some interest in the possibility of diffusing beryllium into iron containing an ultra-fine dispersion of iron oxide. Accordingly, a number of tests have been performed to see how fine an iron oxide dispersion one might obtain in iron. The results look reasonably promising, and are being analyzed in detail to determine whether this process might be of further interest.

Barring the possibility that either of these techniques (above) may yield the desired results, there is available the procedure of mixing ultra-fine beryllium oxide and iron-oxide powders, in the range of 0.1 - 0.2 micron or finer, and then selectively reducing the iron oxide. This laboratory has considerable background in preparation techniques of this sort, and we are prepared to follow this method if it looks more promising than the others.

8. MECHANISM OF DEFORMATION AND FRACTURE OF METAL-METAL OXIDE SYSTEMS

Whereas the great bulk of the work in oxide dispersion strengthened systems has been concerned primarily with the production of structures which lead to high strength properties at high temperatures, there is a lack of understanding of the factors which lead to high or low strength.

values, to high or low ductility, or to good or bad formability. There is little doubt that relatively fine dispersions of oxide in ductile matrices can be produced by a large number of techniques, and unusually attractive high strength properties have been achieved at high temperatures. At the present time, we still do not know whether the fractures are granular or intergranular, through or around the hard particles, etc. Similarly, we are not aware of the role of slip and grain boundary or sub-boundary shear in these alloys. We are also only just beginning to formulate models of the distribution of stored energy in such structures; the recovery of such energy at intermediate and high annealing temperatures; and the distribution of cold work energy either after extrusion or after intermediate annealing treatments.

As a result, if this field is to move ahead at the desired rapid pace, it will be necessary to study deformation and fracture behavior of these materials intensively.

For this phase of our program, we have selected copper as our base material, containing small amounts of aluminum, up to 1 percent by weight, and plan to produce relatively fine powders of these alloys which will be internally oxidized to obtain the most ideal structures possible. Every effort will be made to minimize the number of grain boundaries in these fine powders; efforts will be made to minimize the change in particle size with depth of oxide penetration during internal oxidation by keeping powder particle diameters small; and every effort will be made not to over-oxidize the material whereby copper oxide or excess oxygen in solution in copper might result. It is hoped to produce alloys with oxide interparticle spacings varying from about 0.2 to about 2 microns, thereby to provide a spectrum of structures in which both deformation and fracture can be followed carefully. It is intended, of course, to produce a number of alloys with considerably coarser oxide particles, but this will undoubtedly entail a totally different approach than internal oxidation, and might follow after this program is completed. This work is only just beginning and the necessary alloys are being obtained.

SUMMARY

A total of eight individual research projects are described in this report. The status of these research items is as follows:

1) Internal oxidation of Cu-Ni-Al alloys. Completed by Mr. Michio Yamazaki. A technical report for publication has been written; preprints will be available in several weeks. Based on this study, it will be desirable to improve the powder preparation technique in which case major improvements in strength may be expected.

2) Ni-ThO₂ and Ni-Mo-ThO₂ alloys by selective reduction. Completed by Dr. Jens Rasmussen. A technical report has been accepted for publication by Powder Metallurgy, London. Preprints have been submitted to NASA.

3) Stability and properties of Ni-ThO₂ and Ni-Mo-ThO₂ alloys. Using the same alloys as those prepared in item 2, a Master's thesis was completed by Mr. Gary Ewell. Because his study indicated the nature of the structural instability of Dr. Rasmussen's alloys (which nevertheless gave good low and high strength properties), the work has been extended for several months. Two new alloys have been prepared and are in test. This work will be completed in an additional three months and then reported and submitted as a technical report for publication.

4) Oxide dispersion strengthened niobium. Miss Diane Margel should establish the basic variables which influence the strength and stability of niobium alloys, probably by June 1965. Depending on her findings, a recommendation will be made regarding further work and the potential of the system for high strength, high temperature applications.

5) Recrystallization and stored energy of cold work on the strength and ductility of oxide dispersion strengthened alloys. Dr. Bufferd has completed this research item and a technical report should be forthcoming in the next three months. The findings will undoubtedly be utilized in continuing studies (for example, items 7 and 8, below), because this approach permits total control of stored energy of cold work, texture, oxide stability, recovery, recrystallization. New research projects will be based on this work, but probably not before the summer of 1965, when new students are again available.

6) High volume intermetallic compound-ductile binder structure. Mr. John Benjamin is completing this work and will be finished with this research item in about two months. This work has broadened our understanding of dispersion strengthened alloy systems generally.

7) BeO-Fe alloys. Mr. Frank Hunkeler has only recently started his program, and is studying for his doctorate. The prior efforts reported in the literature with dispersion strengthened iron and iron-base alloys held little hope for strong iron base alloys. Only the as yet unpublished work of Zeilsky, Nelson and Grant (to be published in 1965) on Fe-Al₂O₃ clearly indicated real potential for the system. Mr. Hunkeler will seek to extend the work and to optimize all the processing variables to produce alloys with the same or better degree of strengthening than has been reported for nickel and copper dispersion strengthened alloys.

8) Mechanism of deformation and fracture. Mr. Gary Ewell will continue his studies on this research topic for a doctorate degree (see also item 3). As of now, the alloys are on order for the program described under item 8 in the text of the report.